

Physico-Chemical Changes Taking Place during Manufacture of Condensed Milk

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COLOUR

Relation of Caramelization to Discolouration

Browning of milk is attributed to reaction of sugar in milk. But when solution of sucrose, lactose, dextrose are heated separately, it do not show any sign of browning or caramel flavour. The colour changes in evaporated milk are not in direct relation of time, but it is the reaction of catalytic nature. Similarly, solution of sugar and proteins when heated, a marked brown colour develops and colour could not be removed by washing and also whey is clear showing no sign of any colour.

i. Relation of Amino Acid - Sugar Complex to Browning

- The lactose – protein (amino acid) reaction, responsible for the darkening of milk proteins. The sugar combines with NH_2 group which is alkaline, neutralizing the alkalinity and leaving the acid group free, thereby causing a reduction of pH accompanied by the formation of highly coloured product. It is well known that sugar heated with an alkali turns brown; hence the amino acid - sugar complex which is alkaline would tend to assume a brown colour.

This would be the case especially with a reducing sugar such as lactose, because of the availability of the aldehyde groups, which are naturally present in reducing sugar. This is further proved as if we **add formaldehyde**, (being having a great affinity for amino acid) to evaporated milk at the time of sterilization, **milk remains quite white**.

ii) Effect of steps of processing on Colour

It is found that time and temperature of heating is an important factor contributing towards colour of the milk. In addition it is noted that

1. The time of fore-warming does not show any decisive change in colour. But if it is for long period like 30 min, effect is intense.

2. **Homogenization tends to** diminish the colour of the product because of a **finer sub division of the fat globules** which **prevent such penetration of the rays of light** as it would reveal the butter fat more nearly in its natural colour which is yellow.

3. Storage causes progressive darkening with increase in time and temperature. At (5⁰C) there is no change in colour.

It is observed that **for each 10°C decrease in fore warming temperature, the holding period is increased ~ 2.5 fold** without causing an increase in colour.

Cooked flavour

Heat treatment in processing tends to produce a cooked flavour in evaporated milk. This is also true for fresh milk and milk products in general. It is generally observed that cooked flavour accompanies the darkening of colour. **HTST process produces less cooked flavour than LTLT process.** HTST sterilization treatment (135°C for 0.5 min) reduces the extent of sterilization, decreases the viscosity and also fat separation etc. So because of these limitation factors, **LTLT process is important.**

i) Reaction Involved in Production of Cooked Flavour

It is observed that when heating skim milk, cream, milk, EM, etc., -SH compounds are produced (provided heated to high temperature or at low temperature for longer time) from one or more proteins present. However, **it is found that -SH compounds are wholly responsible for cooked flavour.** Five hours heating at 70°C produces full cooked flavour. It is shown that in the reaction causing cooked flavour of milk by heat, O₂ is taken up and CO₂ is produced. Oxidation condition inhibits the formation of -SH group.

SEDIMENTS OF MINERAL SALTS

There is a tendency in some evaporated milk upon ageing for granular deposit to form in the can. This deposit has a whitish colour, it is gritty and insoluble and seemingly of non-crystalline character. On analysis these granular structure are found to contain Tri Calcium Citrate - $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ and Tri Calcium Phosphate - $\text{Ca}_3(\text{PO}_4)_2$. These salts have peculiarity of being less soluble in hot rather than in cold solution.

i) Effect of Processing on Mineral Salts

The tendency for increased concentration of milk solids to cause an increase in the amount of sediment produced is well known to evaporated milk manufacturers. An increase in concentration necessarily increases Ca, Mg, citric acid and PO_4 content in the milk and thus provides possibility of precipitation. This can be controlled by addition of casein stabilizer.

ii) Effect of Temperature of Storage on Sediment Formation

The precipitation of mineral salts in the form of white sand like deposits is an age defect of Evaporated Milk. The temperature of storage appears to be a controlling factor in this respect.

Effect of temperature of storage on sediment formation in evaporated milk

Time	Temperature	Relative amount of Ca citrate sediment
30 days	29.4	Large amount of fine as well as large particles
78-110 days	20.0	Considerable amount of large particles
4 month	7.2	No sediments

EFFECT OF HTST STERILIZATION

By this process, natural property of milk is retained better than that with the process of low temperature long duration. The **major advantages are to avoid cooked flavour and colour changes**. By HTST sterilization, heat stability will be better in concentrated product than with conventional method of sterilization, but the problems that are encountered in this process are insufficient viscosity and thin body which ultimately increase the tendency of fat separation on storage. Self stability of product is relatively small and gelation may occur during storage period. Some of the different types of processes developed are:

(1) **Tin Sterilization:** Sterilization at 127⁰C-130⁰C for about 2 minutes to 40 seconds.

(2) Continuous Flow Sterilization: Here temperature is 145⁰C or higher with only few seconds holding and with subsequent aseptic canning. For avoiding the problems due to this sterilization process, increase the viscosity and reduce the age thickening.

Several methods are supplementing temperature treatment which may be given before or after sterilization. They may be given to the product during coming up period or cooking period and get the advantage of avoiding cooked flavour.

Effect of Heat Treatment on the Acidity

- When heat treatment is given to milk in manufacture of concentrated milk, the acidity measured in terms of H⁺ concentration and titratable acidity is increased.
- The rate of formation of acid in concentrated product is in proportion of time and temperature treatment.
- If the milk is heated in open pan, then the acidity will slightly drop in the beginning followed by an increase in acidity which will continue till the coagulation of casein. Initial decrease in acidity is due to loss of CO₂ dissolved in milk which usually contributes to 0.01-0.02% of the total acidity expressed as lactic acid. The increase in acidity on further treatment is due to breaking down of casein causing cleavage of phosphorus containing acid, probably nucleic acid and to a lesser extent to oxidation of lactose.

- The actual increase in acidity in SCM is very slight. This slight increase in acidity is compensated by the initial loss of acidity due to expulsion of CO₂.
- In case of evaporated milk, the sterilization heat treatment is more and in addition, the milk is also heated at higher temperature of fore warming. Due to this treatment, usually there is increase in acidity approximately 0.05 - 0.1% during the sterilization process than the normal acidity due to concentration.

i) Effect of Storage, Time & Temperature on Acidity

- The increase in acidity is in direct relation with time and temperature of storage. The acid producing reaction due to heat treatment is continued even when the concentrated product is held in storage room. The rate of acid formation will be very slow depending upon the temperature of storage. SCM of 64.5% sugar ratio having initial acidity of 0.43% and the original bacterial count 4381/g when stored at different temperatures resulted in to increase in acidity is shown in the below table.

Temperature	Time	Acidity
10	640 days	0.84%
15.6	640 days	0.85%
22.2	640 days	1.0%

- This increase in acidity is mainly due to chemical changes as there was no increase in microorganisms during storage.

SWEETENED CONDENSED MILK

i) Age Thickening

- The main change in sweetened condensed milk during storage is presumably age thickening and, finally, gelation.
- Sweetened condensed milk is far more concentrated than evaporated milk. However, it does not thicken markedly faster with age. It is usually assumed that added sucrose inhibits age thickening. Sucrose increases the Ca^{2+} activity. A difference with evaporated milk is that an initial decrease in viscosity before age thickening is not observed. The viscosity in sweetened condensed milk increases almost linearly with time. The following main factors affect age thickening in sweetened condensed milk:
 1. The variation in the type of milk and season occurs among batches of milk.
 2. Higher preheating treatment yields higher initial viscosity, and gel can form earlier. Hence, UHT heating is now generally applied.
 3. The addition of sugar at later stage in the evaporating process results in lesser age thickening.
 4. Higher concentration factor gives more age thickening.

5. The influence of added salts varies widely and depends on the stage at which it is added. Salts are added up to 0.2%. Adding a small amount of sodium tetrapolyphosphate (e.g. 0.03%) mostly delays age thickening considerably, whereas adding more may have the opposite effect.

6. Age thickening considerably increases with storage temperature

ii) Maillard Browning

On going Maillard reactions are inevitable. **Brown discoloration is stronger as the storage temperature is higher**, the milk is evaporated to a higher concentration, and more intense heating is applied. Additional **Maillard reactions occur if the added sucrose contains invert sugar**.

iii) Oxidative Changes

These changes can be prevented by **keeping head space oxygen to a minimum**.

iv) Lactose Crystallization

- **Sweetened condensed milk contains around 38 to 45 g lactose per 100 g water**. The **solubility of lactose at room temperature is about 20 g per 100 g water**, but in **sweetened condensed milk the solubility is about half as much due to the presence of sucrose**. It implies that **75% of the lactose tends to crystallize**, meaning about 8 g per 100 g sweetened condensed milk. **Due to the high viscosity**, nucleation will be slow and only a few nuclei would be formed per unit volume of milk, leading to **large crystals**.

- Without special measures, the product will obtain a relatively high quantity of large crystals. These crystals settle and are **responsible for a sandy mouth feel**. Although the crystals may not be so large as to be felt singly in the mouth, they can be large enough to cause a non-smooth impression. To avoid this, they **should be smaller than about 8 μm in length**.
- Preventing crystallization is not possible and, accordingly, a large number of crystals should be obtained. Satisfactory results can be reached by using seed lactose. Adding 0.03% seed lactose represents 0.004 times the amount of lactose to be crystallized. The final size of the crystals in the product should not exceed 8 μm. Consequently, the seed lactose would contain enough seed crystals (one per crystal to be formed) if its crystal size does not exceed about $(0.004 \times 83)^{1/3}$, i.e., 1.25 μm. Such tiny crystals can be made by intensive grinding of α - lactose hydrate

Physico-chemical changes taking place during manufacture of dried milks

The milk powder manufactured undergo several changes while conversion from liquid milk to dry product. They are:

- § The manufacturing process employed on **milk (~87% water, $a_w=0.99$)** eliminates majority of water till it reaches the final stage of drying, **the powder (~4% moisture, $a_w<0.6$)**. The process not only eliminates the water from milk but also changes the physical structure i.e. the arrangement of the components of milk in space. In the process, the sol changes to a dust.
- § The dried milk exhibits a well pronounced **dual physical structure** – the primary structure, which is **the internal build-up of the powder particles from the milk solids and small amounts of moisture and air** and – the secondary structure which represents a typical powder, **a system of closely packed solid particles in a gas**.
- § The structural elements of dried milk particles are – lactose, either amorphous or partly crystalline, casein micelles and whey protein particles, fat in globular or non-globular (free fat) forms and air as spherical cells. The fat, protein and air are presumably dispersed in continuous phase of amorphous lactose.

§ The whole milk and infant milk powders are rich in fat (20-37%) and hence need protection against oxygen and moisture, therefore, packaging is done under nitrogen cover to replace air with nitrogen in the tins.

§ The milk powders are concentrated mass of milk components in the form of particles with small amount of moisture and air. If sufficient care is not taken to protect them from high humidity, high temperature of storage and the entry of air, the deterioration processes are accelerated.

These changes while manufacture occurs in a sequence. They are discussed here:

CHANGES OF STATE OF THE DRYING DROPLETS

- § Atomizing pure water in a drying chamber in the usual way causes the water droplets to reach the wet-bulb temperature and to vaporize within 0.1 s at this temperature.
- § The presence of dry matter in the droplets, however, makes an enormous difference. The diffusion coefficient of water decrease substantially with increasing dry-matter content. Accordingly, the vaporization is significantly slowed down.
- § In the drying droplet, temperature equalization occurs in less than about 10 ms. i.e. the temperature is virtually constant throughout a droplet during drying.

DRYING STAGES

§ Initially, the droplet has a very high velocity relative to the drying air.

§ Therefore, there is a first stage during which circulation of liquid in the droplet occurs; **this circulation greatly enhances transfer of heat and mass.**

§ For a **droplet of 50 μ m diameter, this stage lasts for ~ 2 ms.** In this time, the **droplet covers a distance of about 10 cm and loses a small percentage of its water.**

§ Its velocity compared to the air decreases to the extent that the formed surface tension gradient of the drop surface arrests internal circulation of liquid.

§ But in the second drying stage, **the difference in velocity between drop and air is still great enough to accelerate water transport.**

§ The **transport in the droplet occurs by diffusion** but in the air by convection.

§ **After about 25 ms the relative velocity of the droplet has decreased so far that the water transport has become essentially equal to that from a stationary droplet.**

§ Relative to the air, the droplet then has covered a distance of a few decimeters and has lost about 30% of its original water.

§ In the third stage, lasting at least a few seconds, the droplet loses the rest of the water by diffusion.

DRYING PROCESS

§ During drying the air temperature decreases and the humidity of the drying air increases. Moreover, the droplets vary in size and the smallest ones will dry fastest.

§ In practice, the mixing is always between the two extremes. In most driers with nozzles, it tends to be closer to cocurrent flows. In all situations, the drying time may vary by a factor of, say, 100 between the smallest and the largest drops. This is of great importance for fouling of the drying chamber; the largest drops have the greatest chance of hitting the wall and of being insufficiently dry to prevent sticking to the wall.

§ Another factor that affects drying rate is the presence of vacuoles in the drying drops. It leads to significantly faster drying.

CONCENTRATION GRADIENTS

A rapid decrease in drying rate of the droplets occurs after the water content is reduced to, say, 15%. A strong concentration gradient forms rapidly during drying. The higher the drying temperature, the stronger the effect. Therefore, stronger gradients occur for cocurrent drying.

The concentration gradients are not of a lasting nature. The relatively dry outer layer of the droplet soon becomes firm and eventually glassy. This causes the droplet to resist further shrinkage. The droplet can react by forming vacuoles or by becoming dimpled. Especially at a low water content of the particles, so-called hair cracks may be formed.

AROMA RETENTION

Besides water, the drying droplets lose other volatile components, including flavour compounds (aroma). In many cases, however, the loss of flavour compounds is far less than expected, in spite of their volatility because of the following conditions:

§ The effective diffusion coefficient of most flavour components in the relatively dry outer layer of the droplet decreases far stronger with decreasing water content than the diffusion coefficient of water does due to the greater molar mass.

§ Thus, the aroma retention - retaining flavour compounds during drying - increases with

- droplet size because in larger droplets, the outer layer from which the flavour components get lost has a relatively smaller volume
- Drying temperature because, at a higher temperature a solid rind forms more rapidly.

§ Formation of vacuoles diminishes aroma retention, especially if hair cracks develop in the particles and the vacuoles come into contact with the surrounding air.

§ Cooked flavour, which results during preheating and possibly during evaporation.

§ During drying, conditions are mostly not such that off-flavours are induced. On the contrary, a considerable part of the volatile sulfhydryl compounds is removed. A cooked flavour mainly results from methyl ketones and lactones formed by heating of the fat and from Maillard products which are almost absent in skim milk powder.

WATER ACTIVITY

If the water content of a product decreases, its water activity (a_w) also decreases. Water activity is expressed as a fraction. In pure water $a_w = 1$; in a system without water, $a_w = 0$.

No	Milk product	a_w
1.	Milk	0.995
2.	Evaporated milk	0.986
3.	Ice cream	0.97
4.	Sweetened condensed milk	0.83
5.	Skim milk powder, 4.5% water	0.2
6.	Skim milk powder, 3.0% water	0.1
7.	Skim milk powder, 1.5% water	0.02
8.	Cheese	0.94 – 0.98

Due to the very low water activity in milk powders, it exhibits following changes:

1. The hygroscopicity increases: Usually, a (dry) product is called hygroscopic if a small increase of a_w causes a considerable increase in water content. Obviously, this mainly concerns milk powder with very low water content.

2. Diffusion coefficients decrease: At low water content the effect is very strong. The diffusion coefficient of water decreases from approximately $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ in milk to $10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ in skim milk powder with a small percentage of water.